

Nitrogen hydrides and the H₂ ortho-to-para ratio in dark clouds

V. Dislaire¹, P. Hily-Blant¹, A. Faure¹, S. Maret¹, A. Bacmann¹, and G. Pineau des Forêts²

¹ Université Joseph Fourier and CNRS, Institut de Planétologie et d'Astrophysique, Grenoble, France

² Université Paris-Orsay and CNRS, Institut d'Astrophysique Spatiale, Orsay, France

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ABSTRACT

Nitrogen bearing species are common tracers of the physical conditions in a wide variety of objects, and most remarkably in dark clouds. The reservoir of gaseous nitrogen is expected to be atomic or molecular, but none of the two species are observable in the dark gas. Their abundances therefore derive indirectly from those of N-bearing species through chemical modelling. The recent years have accumulated data which stress our incomplete understanding of the nitrogen chemistry in dark cloud conditions. To tackle this problem of the nitrogen chemistry in cold gas, we have revised the formation of nitrogen hydrides, which is initiated by the key reaction $N^+ + H_2 \rightarrow NH^+ + H$. We propose a new rate for this reaction which depends on the ortho-to-para ratio of H₂. This new rate allows to reproduce the abundance ratios of the three nitrogen hydrides, NH, NH₂, and NH₃, observed towards IRAS16293-2422, provided that the channel leading to NH from the dissociative recombination of N₂H⁺ is not closed at low temperature. The ortho-to-para ratio of H₂ is constrained to O/P = 10⁻³ by the abundance ratio NH:NH₂, which provides a new method to measure O/P. This work stresses the need for reaction rates at the low temperatures of dark clouds, and for branching ratios of critical dissociative recombination reactions.

Key words. ISM: Astrochemistry, abundances, ISM individual objects: IRAS 16293-2422

1. Introduction

Chemistry in an astrophysical context is not only a matter in itself but also provides invaluable tools to determine physical conditions such as volume density and kinetic temperature (?). Astrochemistry relies on chemical networks which depend on the type of environment (*e.g.* diffuse *vs* dense gas). The kinetic rates of the reactions are, in the best cases, based on thermodynamical and quantum mechanical calculations and experiments, which make the setup of such chemical networks an extremely demanding process. Various such networks of reactions are publicly available (KIDA, UMIST, OSU¹, Flower & Pineau des Forêts²), with various degrees of complexity and/or completeness regarding specific aspects of the chemistry (*e.g.* deuteration, cations...).

The nitrogen element is among the 5th or 6th most abundant in the Solar neighbourhood, after H, He, C, O, and probably Ne (??). In the cold neutral medium, nitrogen is expected to be predominantly atomic or molecular, but direct observations of N or N₂ are not possible. The amount of gaseous nitrogen thus relies on the abundances of N-bearing molecules *via* chemical models. Nitrogen bearing molecules are observed in a wide variety of physical conditions. Molecules such as CN, HCN, and HNC, with large permanent dipole moments, are detected towards diffuse clouds (?), dense cores (?), protoplanetary disks (?) and high-*z* galaxies (?). N-bearing species, such as N₂H⁺ (and its deuterated isotopologues), are also efficient tracers of the dense and cold gas where CO has already frozen-out (???). The cyanide radical CN is also a precious molecule which serves as a tracer of the magnetic fields through Zeeman splitting (?).

Understanding the chemistry of nitrogen is thus crucial in many astrophysical areas.

Ammonia and N₂H⁺ are daughter molecules of N₂, which forms from atomic N through neutral-neutral reactions mediated by CN and NO (?). The formation of CN and the related HCN and HNC molecules, and in particular their abundance ratio CN:HCN, are however not fully understood (?). The formation of ammonia in dark and dense gas is thought to take place in the gas phase. Once N₂ exists in the gas phase, it reacts with He⁺ ions formed by cosmic-ray ionization, to form N⁺ which by subsequent hydrogen abstractions lead to NH₄⁺ and finally NH₃ by dissociative recombination. ? (LB91 in the remainder of the paper) was the first to investigate the influence of the H₂ ortho-to-para ratio (noted O/P) on the formation rate of NH₃. LB91 considered the conversion between *p*-H₂ and *o*-H₂ through proton exchange in the gas phase. He concluded that when O/P ≥ 10⁻³, the formation of ammonia no longer depends on the value of O/P. However, a better test of the nitrogen chemistry is provided by the simultaneous observations of all three nitrogen hydrides, NH, NH₂, and NH₃ (*e.g.*, ?). The Herschel/HIFI instrument has opened the THz window which contains the fundamental rotational transitions of light molecules with large electric dipole moments such as hydrides. ?, Paper I in what follows have detected NH, NH₂, and NH₃ in the cold envelope of the Class 0 protostar IRAS16293-2422. The hyperfine structures of the *N* = 1 – 0 transitions of NH and NH₂ are seen for the first time, in absorption, and allow a precise determination of their excitation temperature (*T*_{ex}) and line centre opacity. Four lines of ammonia are also detected in absorption, plus the fundamental rotational transition at 572 GHz which evidences a self-absorbed line profile, likely tracing both warm and cold gas. For all three molecules, excitation temperatures were found in the range 8–10 K (Paper I). The derived column density ratios are NH : NH₂ : NH₃ = 5 : 1 : 300. Whilst abundances are generally

¹ <http://kida.obs.u-bordeaux1.fr>,
<http://www.udfa.net/>, <http://www.physics.ohio-state.edu/~orange>

² <http://massey.dur.ac.uk/drif/protostellar/>

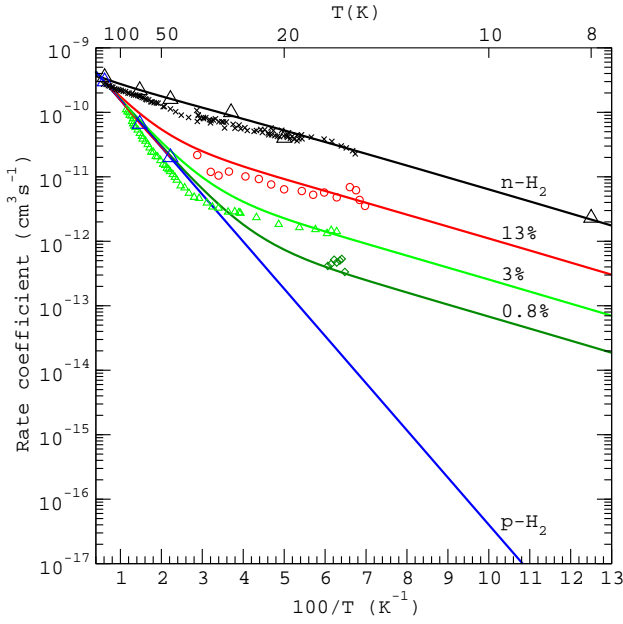
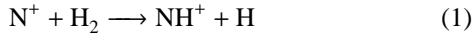


Fig. 1. Comparison of the rate coefficient as given by Eq. 3 to experimental data for the reaction of N^+ with $n\text{-H}_2$ and $p\text{-H}_2$ with different $o\text{-H}_2$ admixtures: 13%, 3%, 0.8%, and 0% (blue line). The small symbols are taken from ? while the large triangles are CRESU results from ?. The solid lines correspond to Eq. 3 of the present paper.

delicate to derive because the column density of H_2 is uncertain, the column density ratios above provide a stringent test for the first steps of the nitrogen chemistry and for the ammonia synthesis in particular. Indeed, the current nitrogen networks available all produce more NH_2 than NH under dark cloud conditions (Paper I), at odds with the observations.

In this Letter, we investigate the $NH:NH_2$ problem in dark gas, by revisiting the kinetic rate for the reaction



We derive separate rates for reaction with p - and $o\text{-H}_2$ for which the nuclear spin $I = 0$ and 1 respectively. In Section 2 we describe the new rates which are compared to experimental measurements and derive the abundances of nitrogen hydrides in typical dark cloud conditions. The results are discussed in Section 3 and we propose conclusion remarks in Section 4.

2. Chemical modelling

2.1. Rate of reaction $N^+ + H_2$

Reaction (1) has a small activation energy in the range 130–380 K (?), with a consensus now tending towards a value below 200 K (*e.g.* ?). This reaction has been studied experimentally by ? who considered pure para- H_2 and a 3:1 mixture of o - and $p\text{-H}_2$, referred to as normal H_2 ($n\text{-H}_2$). These authors fitted the two rates with normal and $p\text{-H}_2$ as $k_n = 4.16 \times 10^{-10} \exp[-41.9/T] \text{ cm}^3 \text{ s}^{-1}$ and $k_p = 8.35 \times 10^{-10} \exp[-168.5/T] \text{ cm}^3 \text{ s}^{-1}$. The rate with $p\text{-H}_2$ was used by LB91, who assumed that the reaction with $o\text{-H}_2$ proceeds with no endothermicity, on the basis that the 170.51 K internal energy of the $J = 1$ level of $o\text{-H}_2$ is used to overcome the endothermicity. Accordingly, the rate of reaction (1) was written as $k_{LB91} = 8.35 \times 10^{-10} [x + (1-x) \exp(-168.5/T)]$, where

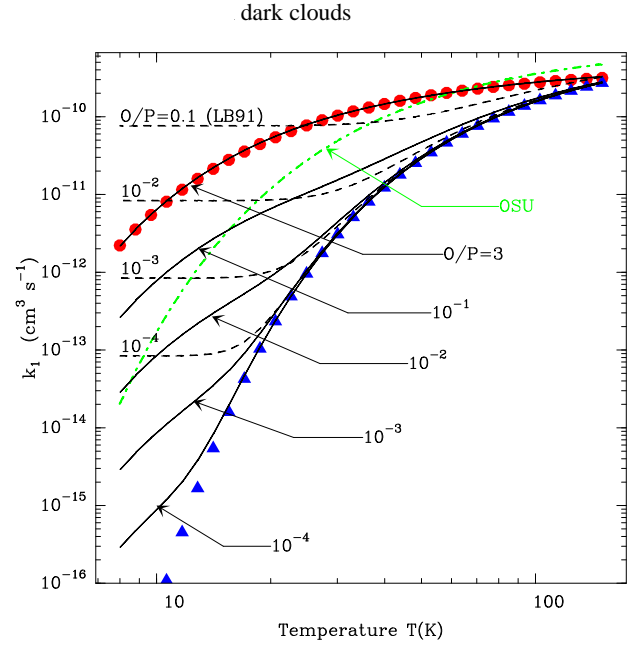


Fig. 2. Comparison of the rate coefficient for reaction (1) as given by Eq. 3 to the rates from LB91 (dashed) and the OSU database (dot-dashed). The rates are computed for temperatures in the range 8–150 K and $O/P = 10^{-4}, 10^{-3}, 0.01, 0.1$, and 3 (black lines). The symbols show the fits from ? for normal H_2 (red circles, $O/P=3$) and $p\text{-H}_2$ (blue triangles).

$x = O/P/(1 + O/P)$ is the fraction of $o\text{-H}_2$. Actually, the expressions for k_n and k_p allow to derive a simple expression for k_o , the reaction rate of N^+ with $o\text{-H}_2$, namely $k_n = 3/4 k_o + 1/4 k_p$ (?). For $O/P=3:1$ and at temperatures less than ≈ 40 K, the rate is essentially k_o , and k_n is thus a good approximation of k_o at the low temperatures ($T < 15$ K) of dark clouds. Alternatively, a single-exponential fit to k_o leads to (see Fig. A.1)

$$k_o = 4.2 \times 10^{-10} (T/300)^{-0.17} \exp[-44.5/T] \text{ cm}^3 \text{ s}^{-1} \quad (2)$$

The rate for reaction (1) with an H_2 admixture of arbitrary O/P is then obtained as

$$k_1 = x k_o + (1 - x) k_p \quad (3)$$

In Figure 1, the rate k_1 from Eq. 3 is compared to the experimental data of ? for the reaction with n - and $p\text{-H}_2$ down to 8 K and 45 K respectively. ? performed experiments with $n\text{-H}_2$ and with $p\text{-H}_2$ containing admixtures of $o\text{-H}_2$ (13%, 8%, and 0.8%), at temperatures down to 14 K. The agreement between our Eq. 3 and the three sets of $p\text{-H}_2$ data of ? is excellent at temperatures below 20 K, and to within a factor of 2 up to 100 K. This suggests that Eq. 3 should be accurate to within a factor of 2–3 down to 10 K. On the other hand, this rate should not be employed above ~ 150 K.

We compare, in Fig. 2, the rate given by Eq. 3 to k_{LB91} and to the rate given by the OSU database $k_{OSU} = 8.35 \times 10^{-10} \exp[-85/T] \text{ cm}^3 \text{ s}^{-1}$. The rate is computed for several values of O/P . As expected, it converges towards the $n\text{-H}_2$ and $p\text{-H}_2$ rates for large ($O/P=3$) and small ($O/P=10^{-4}$) values respectively. It is evident that LB91 overestimated the rate of reaction (1) by several orders of magnitude at temperatures smaller than 20 K. In warmer gas ($T > 20$ K), k_1 and k_{LB91} agree to within a factor of 10 or less, whilst the OSU rate approaches the $O/P=3$ curve. The OSU rate thus amounts to assume O/P ratios larger than 0.01, whereas LB91 provides acceptable rates only at temperatures larger than 20 K.

Table 1. Initial gas phase fractional abundances ($n(X)/n_{\text{H}}$) from ? with $n_{\text{H}} = n(\text{H}) + 2n(\text{H}_2)$. For comparison, the fractional abundances from the low-metal model of ? are also given. Numbers in parentheses are powers of 10.

Species	Flower 2003	Wakelam 2008
H ₂	0.50	0.50
He	0.10	0.14
N	6.39(-5)	2.14(-5)
O	1.24(-4)	1.76(-4)
C ⁺	8.27(-5)	7.30(-5)
S ⁺	1.47(-5)	8.00(-8)
Si ⁺	8.00(-9)	8.00(-9)
Fe ⁺	3.00(-9)	3.00(-9)
Mg ⁺	7.00(-9)	7.00(-9)

2.2. Abundance of nitrogen hydrides

In this work, we wish to reproduce the ratios NH:NH₂:NH₃ observed in the cold envelope of IRAS16293-2422 (Paper I). The fundamental hyperfine transitions of NH, NH₂ and several transitions of NH₃ have been detected in absorption. Absorption is interpreted as resulting from the low temperature of the gas in the envelope seen against the warmer continuum emitted by the dust closer to the protostar. The gas density is low (10^4 - 10^5 cm⁻³) as compared to the critical density of the detected transitions ($> 10^7$ cm⁻³) which ensures that collisions do not govern the (de)excitation processes. The $N = 1 - 0$ transitions are therefore thermalized with the dust emission temperature which, in the THz domain, correspond to excitation temperatures close to a kinetic temperature of 10 K. The lines are Gaussian and do not show signatures of strong dynamical effects such as infall. Dynamical timescales are then expected to be large with respect to the free-fall time. The observed lines therefore trace a cold gas, moderately dense, free of dissociating photons, and where the ionization is driven by cosmic rays.

The main point raised by Paper I is that the observed ratios NH:NH₂:NH₃=5:1:300 could not be reproduced by chemical networks updated regarding the rates of the dissociative recombination (DR) reactions leading to NH, NH₂, and ammonia. Paper I considered three models, with varying branching ratios for some DR reactions. Whilst the NH₂:NH₃ abundance ratio could be reproduced in all three cases, no model was able to produce³ [NH] > [NH₂]. These models used the OSU rate for reaction (1) which was shown in Sec. 2.1 to depart from the measured rate by several orders of magnitude in cold gas and O/P smaller than 0.01. The next Section explores the consequence of the new rate given by Eq. 3 on the abundances of the nitrogen hydrides, in typical dark cloud conditions.

We have performed chemical calculations in a gas at $T = 10$ K, with density $n_{\text{H}} = 10^4$ cm⁻³. The gas is screened by 10 mag of visual extinction, such that the ionization is primarily due to cosmic rays at an adopted rate $\zeta = 1.3 \times 10^{-17}$ s⁻¹. Gas-phase abundances are computed as a function of time by solving the chemical network until steady-state is reached. Freeze-out of gas-phase species onto dust grains are ignored in this work. In what follows, the quoted abundances correspond to the steady-state. The initial fractional elemental abundances ($n_{\text{X}}/n_{\text{H}}$) are the gas phase abundances taken from ?, hereafter FPD03 who considered the depletion of metals in grain mantles, grain cores, and

PAHs (see Table 1). These abundances differ from those adopted in Paper I (?). The rates for the dissociative recombination reactions are those of the model 1 of Paper I. From the above, the rate for the key reaction (1) depends on the O/P which is not known, but which might strongly differ from the thermodynamical equilibrium value (???) which is $\approx 10^{-7}$ at 10 K. The steady-state abundances of NH, NH₂, and NH₃ have thus been computed for various values of O/P in the range 10^{-7} to 3.

In this work, the DR of NH₄⁺ has three output channels, NH₃ + H, NH₂ + H₂, and NH₂ + H + H (?). However, another channel may be NH + H + H₂ (?), but to our knowledge, no branching ratio is available in the literature. Values up to 10% may be considered in a future work.

We first consider the case where the DR of N₂H⁺ produces only N₂ + H (?). The resulting abundances are the dashed lines in Fig. 3. It appears that the O/P controls the abundances of NH, NH₂, and NH₃ but the ratios NH:NH₂ and NH₃:NH₂ are insensitive to O/P. In a second series of calculations, the NH + N channel is given a 10% branching ratio for the DR of N₂H⁺. In this case, the abundance of NH is nearly independent of O/P, while the abundances of NH₂ and NH₃ remain unaffected (full lines in Fig. 3. As a consequence, it is found that for O/P < 0.03, NH : NH₂ > 1. In Paper I though, opening this channel did not solve the NH:NH₂ problem, which contrasts with the above result. This may be understood as follows. When the NH + H channel of the dissociative recombination of N₂H⁺ is opened with a 10% braching ratio, the corresponding rate is $\approx 5.5 \times 10^{-8}$ cm³ s⁻¹, several orders of magnitude larger than k_1 (see Fig. 2). Hence this channel, which is insensitive to O/P, dominates the formation of NH over NH₂⁺ + e⁻. In contrast, the other hydrides NH₂ and NH₃ are daughter molecules of NH⁺ which is formed from N⁺ + H₂ whose rate does explicitly depend on O/P in the present work. Hence the abundances of NH₂ and NH₃ do also depend on O/P. On the other hand, at the temperature of 10 K and O/P < 10^{-3} , the revised rate k_1 (Eq. 3) is at least an order of magnitude smaller than the OSU rate used in Paper I. For larger O/P, the rate is similar or even larger up to a factor of 10. These two effects, namely the drop of k_1 for low O/P, and the O/P-independant formation of NH, makes it possible to produce a NH:NH₂ ratio with values greater than unity. In the following we keep the NH + N channel opened to 10% and explore some consequences of this result.

3. Discussion

3.1. The H₂ O/P ratio in dark clouds

Computing the abundance ratios NH:NH₂ and NH₃:NH₂ for different O/P ratios leads to the left panel of Fig. 4. The initial fractional abundances are kept fixed, while the rate of reaction (1) is calculated for values of O/P from 10^{-7} (close to the Boltzmann value at 10 K) to 3. The calculated ratios are compared with the observational constraints. As expected, the NH₃:NH₂ ratio is insensitive to O/P variations. It is equal to 10, not consistent with the observed value of 300. On the contrary, the NH:NH₂ ratio shows two regimes: for O/P < 10^{-5} , NH : NH₂ \approx 50, and for O/P > 0.1, NH : NH₂ \approx 0.07. The observed ratio of 5 is intermediate, and indeed well constrains the O/P to 10^{-3} . From Fig. 4, we conclude that there is a range of O/P for which [NH] > [NH₂] and [NH] < [NH₃] simultaneously. In our case, this range is O/P = 5×10^{-4} – 0.02. The O/P ratio appears as a control parameter for the NH:NH₂ ratio, and allows for the first time to produce more NH than NH₂. Conversely, the measure of

³ Hereafter, the fractional abundance of species X is noted [X] and equals $n(X)/n_{\text{H}}$.

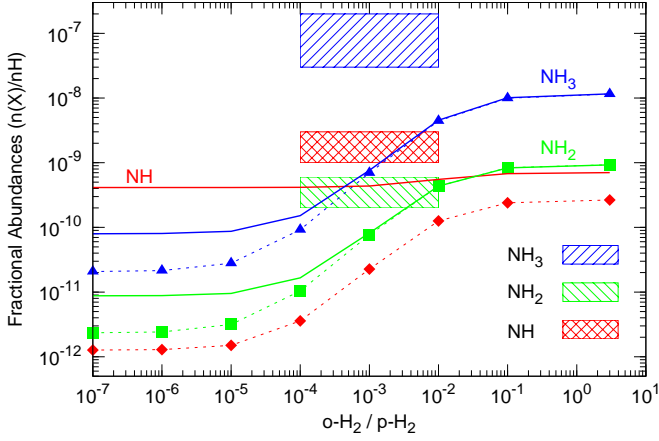


Fig. 3. Steady-state abundances (with respect to H nuclei) of nitrogen hydrides as a function of O/P, in a 10 K gas with $n_{\text{H}} = 10^4 \text{ cm}^{-3}$, and $\zeta = 1.3 \times 10^{-17} \text{ s}^{-1}$. The rate of reaction (1) is given by Eq. 3. Two branching ratios for the channel $\text{N}_2\text{H}^+ + \text{e}^- \rightarrow \text{NH} + \text{N}$ are considered: 0% (dashed lines) and 10% (full lines). The observed abundances from Paper I are also indicated (filled rectangles).

$\text{NH}:\text{NH}_2$ tightly constrains the O/P ratio. We note that the fractional abundance of NH_3 of 1.9×10^{-9} , measured by ? towards the starless core L 1544, corresponds to an $\text{O/P} = 10^{-3} - 10^{-2}$. This ratio is a factor of 10 larger than the corresponding ratio from the model of LB91. It is thus found that reaction (1) regulates the formation of NH_2 and NH_3 whilst the formation of NH is controlled by the dissociative recombination of N_2H^+ provided the branching ratio towards NH is 10%. The value of this branching ratio is uncertain but is likely non-zero (?).

3.2. Dependence on the initial abundances

The $\text{NH}_3:\text{NH}_2$ ratio is ≈ 10 in the above models, a factor 30 below the observed values towards IRAS16293-2422. However, models computed in Paper I with the initial abundances of ? lead to a ratio close to the observed value, hence suggesting that the initial elemental abundances influence this ratio. The gas phase elemental abundances of C, N, and O in dark clouds are poorly known because the amount of these elements incorporated into the dust (core or mantles) is loosely constrained. The elemental abundance of oxygen in the gas phase is not known accurately, and variations by an order of magnitude are fully conceivable (?), whilst that of carbon is better known. Accordingly, we have considered variations of the initial elemental abundances of oxygen, to vary the ratio C:O, encompassing the value of 0.41 from ?.

The resulting abundance ratios, computed for an O/P ratio of 10^{-3} , are shown in Fig. 4 (right panel). As C:O decreases below the 0.66 value of FPdF03, the ratio $\text{NH}_2:\text{NH}_3$ increases. In the process, $\text{NH}:\text{NH}_2$ remains constant. When C:O is now increased above 0.66, both ratios decrease, by at most a factor 2 to 5. It is thus apparent that, when [O] is increased, the C:O ratio controls the $\text{NH}_2:\text{NH}_3$ ratio. On chemical grounds, the C:O ratio is expected to influence the abundance of NH_2 , for which the main destruction routes involve oxygen to form NO, NH, and HNO. Similarly, NH is mostly removed by reaction with oxygen to form principally NO. However, when oxygen is significantly depleted from the gas phase (C:O > 0.5), another destruction

route of NH, involving sulfur, becomes important. As a result, the $\text{NH}:\text{NH}_2$ ratio is mostly insensitive to C:O, until $\text{C:O} > 0.5$ when it starts to decrease by small factors.

The situation is different for NH_3 which is destroyed by charge transfer reactions with H^+ and S^+ and by proton exchange reactions with H_3^+ and HCO^+ , forming notably NH_4^+ , which dissociates back into NH_3 , and NH_3^+ . A fraction of NH_3^+ will lead to NH_2 and NH which are the true destruction channels of ammonia. The abundance of NH_3 is thus only marginally affected by the change in C:O, unless the ionization fraction is modified, which is the case for low C:O ratios. An increase of the oxygen abundance (*i.e.* a decrease of C:O) is accompanied by a decrease of $[\text{e}^-]$, or equivalently $[\text{S}^+]$ – the dominant ion – which makes the abundance of NH_3 to increase. Consequently, as C:O decreases below 0.66, $\text{NH}:\text{NH}_2$ keeps constant and $\text{NH}_3:\text{NH}_2$ increases by more than one order of magnitude. Whereas when C:O increases, $\text{NH}:\text{NH}_2$ decreases by less than a factor 10, whilst $\text{NH}_3:\text{NH}_2$ is approximately constant.

4. Conclusions

Using an updated rate for reaction (1) with an explicit dependence on the O/P ratio, we have shown that the O/P of H₂ controls the ratio $\text{NH}:\text{NH}_2$ in dark clouds without affecting the $\text{NH}_3:\text{NH}_2$ ratio. A value of O/P close to 10^{-3} leads to $\text{NH}:\text{NH}_2 > 1$ and $\text{NH}_3:\text{NH}_2 < 1$ as observed. Interestingly, this value of O/P is close to the predictions of ?, their Fig. 1 under similar conditions. In addition, measuring the $\text{NH}:\text{NH}_2$ ratio may be a new method to constrain the O/P ratio of H₂ in dark clouds. We have also shown that decreasing the C:O ratio by increasing [O] controls the $\text{NH}_2:\text{NH}_3$ ratio. Finally, acceptable parameters are found that lead to abundance ratios in agreement with the observations towards IRAS16293-2422, namely $\text{O/P} \approx 10^{-3}$ and $\text{C:O} \leq 0.4$. It is to be noted, however, that in this range of parameters, the absolute abundances predicted by the models are a factor of 10 below those derived in Paper I.

In this work, the influence of O/P on the ratios $\text{NH}:\text{NH}_2:\text{NH}_3$ has been explored only through the rate of reaction (1). A better study would be to self-consistently compute the O/P ratio from a model of conversion of o-H₂ into p-H₂, as was first considered by LB91, and more recently by *e.g.* ?. Including proton exchange reactions, in the gas phase, between H₂ and H^+ (?), H_2^+ (?), and H_3^+ (?), would reprocess the 3:1 mixture of H₂ formed on grains to a different O/P. An even more self-consistent approach would be that of ? who separate reactions with the ortho- and para- forms of all concerned N-bearing molecules. Another obvious continuation would be to explore these findings in different physical conditions (A_{V} , cosmic-ray ionization rate, *etc.*).

Branching ratios of dissociative recombination reactions are crucial to the formation of nitrogen hydrides. In this work, the dissociative recombination of NH_4^+ has three output channels $\text{NH}_3 + \text{H}$, $\text{NH}_2 + \text{H}_2$, and $\text{NH}_2 + \text{H} + \text{H}$ (?). However, another channel may be $\text{NH} + \text{H} + \text{H}_2$ (?), but to our knowledge, no branching ratio is available in the literature. Values up to 10% may be considered in a future work. Critical too are the values of rates at low temperatures, especially for reaction (1) with p-H₂ for which measurements at temperatures lower than 14 K are not available.

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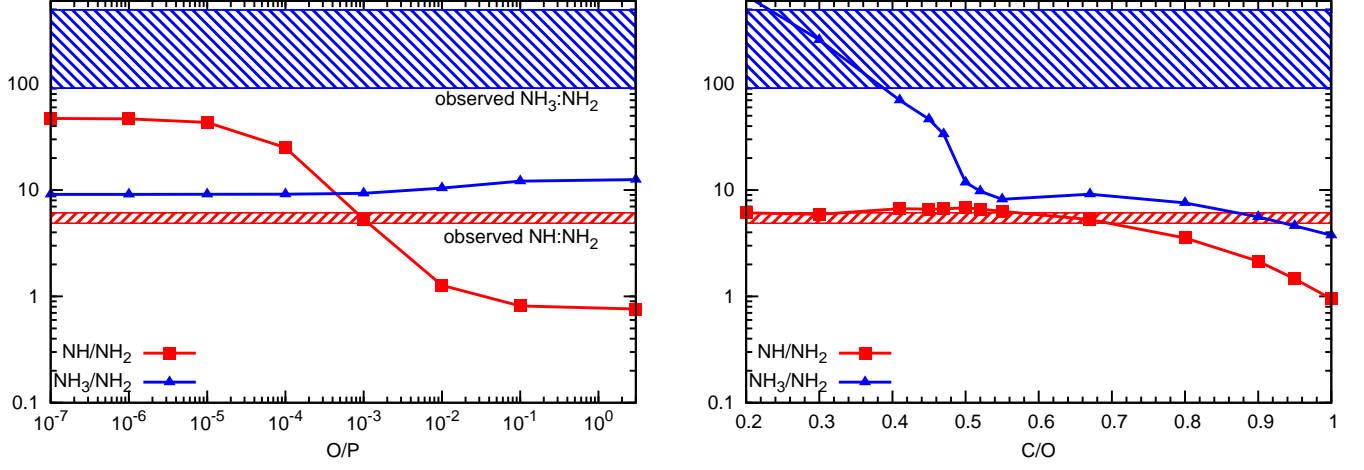


Fig. 4. Abundance ratios calculated when a 10% branching ratio is considered for the reaction $\text{N}_2\text{H}^+ + \text{e}^- \rightarrow \text{NH} + \text{H}$. The hashed bands show the observed ratios with their 1σ uncertainties. *Left panel:* varying O/P, with the initial abundances of ? ([O]=1.24(-4) and [C]=8.27(-5)). *Right panel:* varying [O] while keeping [C] constant, at constant O/P=10⁻³. The low-metal abundances of ? are [O]=1.76(-4) and [C]=7.30(-5), or C:O=0.41.

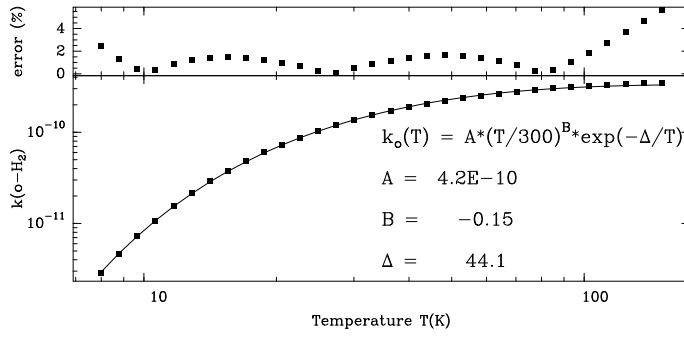


Fig. A.1. Rate for reaction (1) with o-H₂ and fit result (see Eq. 2). Bottom panel: filled squares are the values derived from ?, and the fitted curve (full line). Top panel: relative error.

Appendix A: Reaction rate

For the purpose of implementing the rate of the reaction (1) with ortho-H₂ in chemical networks, Figure A.1 shows the result of a single-exponential fit. The filled squares are based on the fitted reaction rates from ?. A weighting in the form $1/(T - 10)^2$ was adopted, which is accurate to better than 6% for $T = 8 - 150$ K.